1971

Permeability to water of polyethylene films grafted with styrene

Narasimhan Chander
Lehigh University

PERMEABILITY TO WATER OF POLYETHYLENE FILMS GRAFTED WITH STYRENE

by

Narasimhan Chander

A Research Report

Submitted in Partial Fulfilment

of the Requirements for the degree

of

Master of Science

in

Chemical Engineering

Lehigh University
Bethlehem, Pennsylvania 18015

June, 1971

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

5/28/71
Date

J. A. Manson,
Professor-in-Charge.

L. A. Wenzel,
Head of the Department.

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PERMEABILITY TO WATER OF POLYETHYLENE FILMS GRAFTED WITH STYRENE

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ABSTRACT

This report describes the preparation of poly(ethylene-g-styrene) by irradiation methods and the permeability characteristics of the graft polymer to water at desalination process temperatures and pressures. The films are potential candidates as barrier membranes to protect concrete against corrosion during the desalination process.

It was found that filling up the holes in polyethylene by styrene monomers did not restrict the permeation of water, at temperatures ranging from 25-80°C. It seems likely that the morphology is altered by the grafting so that a more open texture is obtained. Thus, we have a slightly enhanced permeation in graft polymers, as compared to plain polyethylene.

I. Introduction

(a) Purpose of the Study

The research work presented herein was sponsored by the Office of Saline Water, U. S. Department of the Interior, Washington, D. C. The OSW is concerned with the many facets of desalination, from the fundamental theories to the practical application of these theories in the desalting of sea-water for potable use.

Among the many methods available for desalting, there is the relatively simple process of flash distillation. With the use of pipe stills, which consist of tubing arranged in a furnace setting, the brackish water is heated until a sufficient temperature is reached to vaporize part of the feed. The vapor remains in contact with the remaining liquid until the exit of the pipe still. Through the pipe still tubes, a considerable pressure drop may develop, depending on the degree of vaporization. At the exit of the tubes, the flow enters a flash distillation chamber which is considerably larger than the tubing. The effect is to reduce the pressure of the liquid and make the latent heat of vaporization available from the sensible heat of the liquid. The result is additional vapor or flashing.

It has been suggested that concrete be employed as the material of construction. (There could be other alternate

materials, but we are dealing with the protection of concrete). It would give a considerable savings in cost. However, a protective coating is necessary for concrete because it is highly susceptible to corrosion from salt and water; the two effects from exposure to marine (saline) water are (1) leaching of CaO causing the structure to crumble, (2) exchanging of the cation with the sulfate ion causing expansion and stress in the concrete.

The main objective of the program, of which this study forms a part, is to investigate the possibility and feasibility of polymer coatings to protect concrete.

The distillation chamber needs a life of 20 to 30 years with exposure to sea-water at 290°F and elevated pressure. There is the difficulty, both economically and physically, of replacing the corroded, crumbled cement walls when allowed to stand bare against the strong saline environment's ravaging attack. To alleviate and lessen the handicap, we are trying to build a barrier that protects the concrete from such hazards.

This report deals with the characterization of graft copolymers with regard to their permeability to water. We have proceeded along a chosen line for the synthesis of our polymer and have studied its susceptibility to saline environments. Plausible explanations are offered. Clearly, further work and discussion on these and related problems are required.

The reason for choosing a graft co-polymer runs as follows: Polyethylene is a good barrier to the permeability of water. It has found increasing applications of it in consumer-oriented packagings. Meat-wrapping, for instance, offers an example of its use, where one needs a wrapper that can breathe oxygen to keep the meat fresh, but which can restrict the permeation of water or water vapor.

Fels & Huang (1) claim that it is the free volume in the semi-crystalline polyethylene polymer that permits transmission of liquids through the film. If there could be a method to reduce this free-volume, it would consequently reduce the permeation of liquids. This idea is consistent with a free volume theory originally proposed by Fujita (3).

Myers (2) claims that irradiated polyethylene has a reduced permeability to nitrogen gas. Later, Myers did the same experiment on grafted polyethylene and found it to substantially reduce permeability. The grafting monomers used were styrene and acrylonitrile. The next chapter deals with an exhaustive report on this and similar reports in the literature.

Fels & Huang have similarly grafted styrene monomer to polyethylene by the simultaneous irradiation technique and find that this enhances permselectivity. Michaels and Bixler (15) further extol the effects of annealing on permselectivity to binary liquids.

The process of grafting we chose is the one which Ballantine claimed to yield the most homogenous type of film possible.

Finally, a timely paper by Connolly (4) is worth noting. He studied the effect of sea-water on polyethylene during an exposure duration of 15 years, and found very little effect. This confirms our supposition that polyethylene should be a reasonable barrier, at least at low temperatures.

(b) Literature Survey

(i) Diffusion and Solubility

The free volume theory of diffusion has been extended to polymeric systems by H. Fugita (3). The basic idea is that the mobilities of both the polymer segment and the diffusing molecule in a polymer-diluent system are primarily determined by the amount of free volume present in the system. The "free volume" is analogous to the "hole" which is opened up by the thermal fluctuations of the polymer system and is expressed as a function of the total volume of the system.

Before we proceed further, let us define a permeability constant, P, as

$$P = D.S$$

where D is the diffusivity of the system and S is the solubility of the permeant in the membrane. From the plots of permeability and temperature (^{o}K), diffusivity and temperature, it could be said that they have an Arrhenius type of relation, such as,

$$P = P_o\, e^{-E_p/RT}$$

$$D = D_o e^{-E_d/RT}$$

and hence, $$S = S_o e^{-\Delta HS/RT}$$

where

P_o is the Permeability constant

E_p is the Activation Energy required for Permeability

R is the Universal Gas Constant

T is the Temperature in ^{o}K

In two papers by M. Fels and R. Y. M. Huang (1,5), the free volume theory has been used to determine the diffusion coefficients of liquids in polymer membranes. They have studied the effect of styrene grafting on the diffusion and solubility of organic liquids in polyethylene. The Fujita free volume express is:

$$\frac{D_T}{D_{c=o}} = \text{In} \left[\frac{\nu_p}{[f(0,T)]^2 \beta_d + [f(0,T)/B_d]\ \nu_p} \right]$$

where D_T is the thermodynamic diffusion coefficient

$D_{c=o}$ is the diffusion coefficient at zero concentration,

ν_p is the volume fraction of the diffusing species,

$f(0,T)$ is the free volume of the polymer at temperature T

$\beta(T)$ is a proportionality constant relating the increase in free volume of the system with added liquid

β_d is a constant for a given system and is related to the size of the minimum "hole" for a diffusional step to occur.

(ii) Permeation in Graft Copolymers

Fels & Huang prepared their graft copolymer of styrene onto polyethylene film by simultaneous irradiation-cum-grafting. They report their study of change in $D_{c=o}$ with percentage grafting. Their report indicates (from their graph of $D_{c=o}$ vs percentage grafting) that $D_{c=o}$ decreases with increasing per-

centage grafting. This therefore indicated that the free volume parameter of the polymer network available for diffusion decreased as more styrene was grafted. However, they warn that $D_{c=o}$ also depends on the morphology, history of film preparation, etc.

Their explanation for the reduction is as follows. When graft co-polymerization takes place at the free radical sites on the polyethylene backbone, the polystyrene attaches itself onto the polyethylene chains in the amorphous regions. In this way the mobility of the polymer chains is reduced, resulting in a lowering in the free volume.

Fels and Huang further note that conditioning of the film by soaking in the penetrant liquid did not appreciably alter the crystallinity measurements. They note that in their experiments, below a grafting percentage of 26%, grafting took place at the amorphous contents where it would affect the free volume for diffusion. The grafted polystyrene is considered to be analogous to "cross-links". The effect (apparent) of cross-linking appeared from the randomly coiled side chains becoming entangled with other molecular chains. One caution in interpretation was stated. The free volume of the polymer depends to some extent on the permeant used in the desorption experiment.

Raff and Allison (6) describe the permeability of gases and vapors through elastic and plastic membranes as a combination of the 2 functions of solution and diffusion. The process is that the gas first dissolves in the polymer, then diffuses through to a position of lower concentration, and then evaporates from the other side.

In describing the effects of radiation on membranes (6, p.138). Raff and Allison say that 90% of the gases liberated during an in vacuo irradiation of polyethylene is hydrogen gas. They further conclude that 'in vacuo' irradiation of polyethylene eliminated its cold-drawing properties, made it more brittle and more like a three-dimensional polymer due to (cross-linking). They report that there was a reduced permeation to gases due to this in vacuo irradiation (actually, a reduction in the diffusion constant). In one of their cross-references, a distinguished worker, Chapiro, says that irradiation could always lead to either cross-linking or degradation.

An article (7) by Myers, Rogers, Stannett and Szwarc supports the possibility that poly(ethylene-g-styrene) could have a lower permeability than a homopolymer of ethylene. They found that the flow rate of gas permeation could be given as:

$$\frac{\partial v}{\partial t} = -P.A.\left(\frac{\partial p}{\partial x}\right)$$

where permeation P is in cc gas(STP)/cm^2.mm/sec/cmHg

$\frac{\partial p}{\partial x}$ = partial pressure gradient across the film

A is the area of the film in cm^2, and the flow-rate is expressed in cc STP/Sec.

Myers et al show that there is a small decrease in the permeation of gases in poly(ethylene-g-styrene) for low levels of grafting, followed by an increase for high levels of grafting. Myers also agrees about the decrease in free volume for low-levels of grafting. He points out that at higher levels of grafting there is a decrease in crystallinity which leads to increased permeation - since permeation is through the amorphous or low percentage crystalline areas.

A 'relaxation' process is cited as the reason for the small decrease in the low-graft regions. The relaxation follows the treatment of highly crystalline polymer in a good swelling agent such as styrene.

Myers' results with acrylonitile grafts (in place of styrene grafts) showed no such minima in permeability. Of course, we should remember that all these permeations deal with gas permeations. He finds a continued reduction in the gas permeability till a 100% or more acrylonitrile % of grafting is reached.

Myers et al feel that the grafted polyethylene in this

case is more tightly coiled in the hydrocarbon matrix as compared to plain polyethylene. Thus, it would be more impermeable. They claim that this does not happen in the case of styrene grafts.

An interesting and similar study was made by Huang and Kanitz (8). They studied the permeation of gases through modified polymer films in general and graft copolymers in particular. The system they chose was, coincidentally, polyethylene-styrene graft copolymer. A brief summary of their findings is in order. The permeability of polyethylene did not significantly change with irradiation, up to a close of 10 Mrad. However, graft copolymers of the same polyethylene showed a reduced permeability with increasing graft concentration, till it reached an optimum. Later, the permeability actually increased with increasing graft concentrations.

The activation energy, Ep, decreased from 11.7 K cal/mole for plain polyethylene to 9.5 K cal/mole for a 50.5% styrene graft. The gas used was nitrogen.

Huang and Kanitz, in order to explain the grafting mechanism, suggest that, though the free-radical sites are formed throughout the irradiated film, there is some difficulty on the part of styrene to actually diffuse through to all the inner sites, especially the crystalline regions. It is assumed that most of the grafting occurs at the amorphous

regions. Mere cross-linking of polyethylene with a dose of less than 10^7 rad has little effect on the permeability of gases.

In the region of 20-30% grafting, a minimum in P was found. It was pointed out that if the equation P=D.S holds, P depends on both D and S, either of which could depend on structural changes.

Due to the presence of grafted polystyrene, the solubilities of nitrogen, oxygen and carbon-dioxide were somewhat higher than in polyethylene, depending on the amount of grafting.

Taking the cue from Fujita (3), Huang and co-workers say that the initial decrease in the permeability constant with percent grafting could be explained in terms of a decrease in the free volume and segmental mobility of the amorphous regions. The grafted polystyrene renders the polyethylene chain segments less mobile and increases the cohesive forces opposing hole formation, resulting in a decrease in diffusion and permeation rates.

The sudden change in P in the 20-30% graft range and the increase in P with increasing percentage grafting has been explained by Huang and Kanitz as follows: It could probably be due to the changes in the amorphous-crystalline ratio. Above 20-30% grafting, the polystyrene chains penetrate and disrupt some of the crystalline regions of the polyethylene and open up new regions made available for increased gas permeation.

In yet another paper, Huang and Jarvis (9) talk about the separation of liquid mixtures by using polymer membranes. Though this is not of immediate interest to our project, a few highlights might heighten our interest. Close boiling mixtures could be separated by polymer membranes. Binary liquid mixtures of different polarity were selectively permeated. Cellophane film, boiled in water, preferentially passed water from a water-alcohol solution.

In a theoretical model, they say that water has a plasticizing effect and also that water-clusters are formed within a polymer when used for permselection. The water, in its role as plasticizer, helps in loosening and swelling the polymer structure and allows the polymer segments to move more freely about the backbone.

Clusters, which are nothing but the mutual association of water molecules, tend to take a lesser part in the diffusion than unassociated molocules, due to the relative immobility they gain. Thus this immobility tends to inhibit diffusive jumps. As a result, the rate of diffusion can be expected to decrease.

A. Furuhashi and M. Kadonaga (10) suggest a continuous flow of monomer vapor for grafting. They say that hardly any homopolymer could be formed. In polyethylene grafts the

concentration is homogenous throughout but there appears a retardation (low concentration) at the surface. In polypropylene-butadiene grafts, a concentration gradient from one side to the other was noted. Matsuo is quoted as saying that as the monomer concentration increases, the graft concentration on the surface decreases. The decrease of this effect in the liquid phase grafting reaction may be attributed to the fact that the monomer concentration is almost homogeneous throughout the material.

We should now look into the process by which pre-irradiated graft reactions occur. There are 2 effects of gamma irradiation upon polymers: (i) the random loss of side groups, such as hydrogen atoms, from the polymer chain and (ii) main chain fracture to give polymeric radicals.

(1) $\sim CH_2-CH_2-CH_2\sim \xrightarrow{\gamma\ ray} \sim CH_2-\dot{C}H-CH_2\sim$

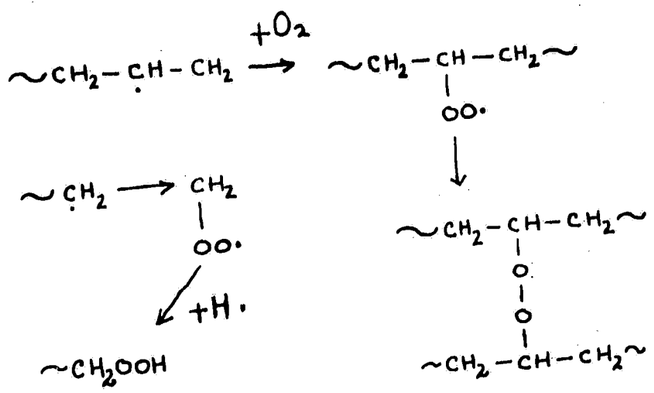
(2) $\sim CH_2-CH_2-CH_2\sim \xrightarrow{\gamma\ ray} \sim CH_2-\dot{C}H-CH_2\sim$

$\therefore$ (1) + (2),

$$\longrightarrow \sim CH_2-\underset{\sim CH_2-CH-CH_2\sim}{\underset{|}{CH}}-CH_2\sim + H_2\uparrow$$

at low temperatures, trapped radicals are formed due to the immobility of the polymer chains. Absence of oxygen is essential. Hence, in vacuo treatment gives trapped free radicals at low temperatures.

In the presence of oxygen, peroxide and hydroperoxide linkages are formed,



(iii) Preparation of Graft Polymers by Irradiation.

Ballantine et al (2) grafted styrene onto polyethylene (low-density) by 4 different methods, using gamma-irradiation.

1. Simultaneous Grafting (a) Film irradiated while immersed in monomer

   (b) Irradiation of monomer-swollen film.

2. Post-Irradiation Grafting (a) Pre-irradiated in air.

   (b) Pre-irradiated in vacuo.

In both 2 (a) and 2 (b) irradiation is followed by the addition of monomer.

Ballantine and co-workers used the same system of polyethylene and styrene for all 4 techniques and found by photomicrographic studies that method 2 (a) gave the most homogenous type of graft, with the least amount of homopolymer of styrene. When irradiated in air, peroxides are formed, whereas trapped free-radicals are produced when irradiated in vacuo. Hydrogen gas is produced and escapes out of the film by diffusion. Any cross-linking of the polyethylene is discounted by the author. He is further of the view that free-radicals are located within the crystalline regions where the mobility of polymeric segments will be low.

It was with a view to produce the most homogenous graft co-polymer that the technique of pre-irradiation in vacuo was undertaken in this study.

Iv. Gamma Irradiation Theory

Radiation chemistry deals with the chemical changes produced by high-energy radiations as opposed to radio-chemistry which deals with the study of radio-active elements.

The high-energy radiations with which radiation chemistry deals with include the electromagnetic radiations of wavelengths below 100-1000°A i.e. of energy greater than 10-100 ev.

One of the characteristic properties of high-energy radiation is to cause ionization of the medium in which it is absorbed. Hence, the term "ionizing radiation". High-energy radiation often converts stable molecules into free-radicals. Since free-radical chemistry is a well defined kinetics field, radiation chemistry forms a part of it.

Gamma-Rays: Electro-magnetic radiations originating from the atomic nucleus and having wavelengths below 100°A are called x-rays. The mechanism of the interaction of the x-rays with matter is explained by Swallow (13). Gamma rays lose their energy mostly by Compton scattering and to a lesser extent by pair production and photoelectric absorption.

In the Compton effect the incident x-ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy.

The electron and photon interact subsequently with the material being irradiated, and give rise to essentially two

processes - ionization and excitation. In the case of ionization, the Compton electron transfers sufficient energy to the orbital electron of another atom to overcome the forces binding it to the nucleus. The electron is therefore ejected, leaving behind a positive ion. If the energy transferred is insufficient to cause ejection of an electron, the energy level of the atom is raised and the atom is said to be in an excited state. The ions and excited molecules are very reactive; they either eract with other materials present in the system or decompose into radicals and atoms or molecules. The free radicals produced upon irradiation of polymeric systems may be used to initiate graft polymerization.

2. Experimental

(a) Description of the Apparatus

(i) Vacuum System

The vacuum-line (see Fig. 1) was fabricated from Pyrex glass tubes and ground-glass tubes (#1,2). A Macleod gauge which showed pressures as low as 5μ of mercury was attached to the system at one end. At the other end a 0.5 hp vacuum pump was attached. The line could be either connected directly to the vacuum pump or indirectly to a mercury molecular diffusion pump, as required.

(ii) Insertion of samples

The polymer and monomer samples were polyethylene film and liquid styrene, respectively. As in figure 1, they were placed in tubes 1 and 2, respectively. The film was rolled to exactly fill the inner wall in a hollow, cylindrical manner. The liquid styrene in 2 was filled just below the brim. Both the lower tubes in 1, 2 were matched to their corresponding ground-glass joints and the vacuum pinch cock opened or closed, as desired. Heavy rubber tubing was used to connect the tubes to the line.

After reaching a vacuum equivalent to a pressure of 10μ of mercury, the diffusion pump was used to achieve still lower pressures.

The irradiation technique is described in (iii) below.

(iii) The Irradiation Source

The Gamma-cell (Gamma-Cell 220) contains Co^{60} which emits 1.17 and 1.33 Mev x-rays and has a half-life of 5.3 years. Co^{60} is usually supplied as cobalt metal contained in a capsule to eliminate the spread of activity. The dose rate at the center is approximately 0.5 Mrad/hr.

Gamma-ray sources above a few hundred millicuries (the Gamma Cell 220 has 12012 curies) require special shielding, and for this purpose lead containers are used. They are heavily designed against the spread or leak of activity. Hence the main irradiation chamber is a hollow cylinder that juts out of the cell for the removal or placing of the material. On pressing an electrical timer, it slides back inside the cell whence it is exposed to the Co^{60} source. It pops up as the time set by the timer expires.

(iv) Permeability Apparatus

The permeability cell and the pressure cell are as shown in William Flis' work (11). Made of Monel metal to precent corrosion, they are also designed to withstand high pressures, say, up to 1000 psig. The high pressure side has a nitrogen gas cyclinder connected to the pressure cell at a definite pressure (50 psi). The low pressure side uses nitrogen as a sweep gas, drawn from a separate cylinder and flowing at 20 psi & 100 cc/min. This gas goes to the moisture-monitor. The film to be tested lies on a porous metal base as shown in the figure. A complete description is given by Flis (11).

The moisture content of the effluent gas was measured using a CEC 26-301 moisture monitor, which operates on the principle of analysis by electrolysis. The analysis is accomplished by continuously absorbing andelectrolyzing all water present in the sample stream entering the instrument. The electrolysis current, which is related directly by Faraday's Law to the mass rate-of-flow of water into the instrument, is used to accurately indicate the sample's water content. Because changes in sample-flow rate, as well as changes in concentration, affect the mass-rate-of-flow of water into the analyzer, the flow is kept constant by using a flow controller. The indicated current is thus proportional only to the water concentration, expressed conveniently in parts per million by volume.

The moisture monitor is a precise instrument designed to measure moisture in a gas at concentrations from 1 to 1000 parts per million, the gas flowing through the unit at 100 cc/min. It can also measure the dew point in such gaseous flows.

The heart of the instrument is the electrolytic cell which has a sole function of responding to water and water alone. However, corrosive gases and liquids might damage the instrument if sent through for analysis. The CEC manual describes such gases and also warns of interference from dirt.

(b) Impregnation Technique:

The procedure for grafting styrene in a film of polyethylene could be achieved in four ways, as mentioned earlier. We followed the procedure of pre-irradiation of polyethylene in vacuo, followed by contact of styrene monomer, also in vacuo. Styrene monomer is allowed to diffuse through the irradiated film of polyethylene whereby styrene is grafted onto the free-radical sites that have been created by gamma irradiation.

Low-density polyethylene of 4 mil thickness (Ethyl Corporation) was used in our experiments. Pure liquid styrene of Borden Chemicals was used as the monomer. The polyethylene was placed in the sample tube and de-gassed by connecting to the vacuum-line. De-gassing was done both at room temperature (25°C) and at a very low temperature attained by liquid N_2 bath. The limiting pressure reached was 5μ of mercury. Similarly, styrene was purified and the inhibitors removed by vacuum-distillation.

The polyethylene was then removed from the vacuum-line and taken to the Gamma cell. It was irradiated from 1 to 5 hours at a temperature of 25°C. The source had an approximate dosage rate of 0.5 Mrad/hour.

The polyethylene was then brought back from the Gamma cell and readied for contact with styrene. During the pre-irradiation in vacuo, due to the free-radical reactions:

some H_2 and other gases were formed. These had to be purged to create a vacuum equal to that in the styrene section of the system. After de-gassing of hydrogen, both at room-temperature and liquid N_2 temperature, the tube containing styrene (at room temperature) was connected to the tube containing the irradiated polyethylene by opening the vacuum stop-cock. This step was done rapidly so as not to lose much time for the trapped free-radicals to decay with time. As an added precaution, pre-irradiated polyethylene was kept at a super-cooled temperature throughout the contact with styrene monomer. The contact time was 7½ hours. A cold temperature reduces the mobility of free-radicals in the polyethylene and also helps in the diffusion of styrene onto polyethylene by a thermal potential gradient.

The styrene vapors emanating from the styrene section and entering from the top of the film (which is vertically rolled along the inner surface of the cylindrical glass-tube) deposited as frozen solids due to the outside liquid nitrogen bath. The frozen styrene however soon melted down and flowed along the surfaces of the film to the bottom of the tube as a liquid because of the evaporation of the liquid nitrogen in the outside bath. Contact was continuous for 7½ hours.

After 7½ hours, the polyethylene tube was removed from the vacuum-line and opened to atmospheric pressure. The liquid styrene that submerged the film was drained and the

film washed with benzene several times. The film was soaked in benzene overnight to dissolve both ungrafted polystyrene and styrene monomer that might have had diffused in but remained unreacted. The film was vacuum-dried to remove benzene and weighted for change in weight.

The percentage styrene grafted was denoted as $\frac{W_2 - W_1}{W_1} \times 100$. Tests showed that the density of specimens cut from various portions of the film was reasonably uniform, to within $\pm$ 0.01 gm/ml.

Measurements

(c) Permeation:

The permeability coefficient P, of a sample is an Arrhenius type of function denoted by

$$P = P_o e^{-Ed/RT}$$

or

$$\ln P_o = \ln P_o - \frac{E_d}{RT}$$

and $P = D \times S$

Where D and S are the diffusion and solubility coefficient, respectively. P is a function depending on the factors like concentration, flow-rate of a purging gas, thickness of film and area of film, and the temperature of the system (^oK). A plot of P vs 1/T will give the apparent energy of activation, for the permeation process (semi-log paper).

Annealing

To further improve the lowering of permeability of the samples, and to approach an equilibrium state, we annealed all the samples at 70°C in tap water for 24 hours. This again formed a basis for all our calculation. With a few exceptions, results are thus based on annealed polymers.

The film was mounted in the permeability cell between two hollow Monel metal plates and with a porous plug of iron base for the film to rest on. The permeability cell was connected to the pressure cell which delivered a certain pressure to the tap water diffusing through the film. The pressure cell's pressure was obtained from a nitrogen gas cylinder having a pressure-gauge. The pressure delivered was maintained at 50 psig.

On the low-pressure side of the film, a second nitrogen gas cylinder was used to sweep permeated water, at a pressure of 20 psig and a constant flow-rate of 20 psig. This gave a pressure gradient of 30 psig.

The whole system (excluding the gas cylinders) was housed in a thermostat-controlled oven, which heated the system at temperatures up to 100°C with a precision of $\pm$ 0.5°C.

The diffusing water molecules vaporize in face of the purging nitrogen gas, which carries the water through the moisture monitor. The electrolytic cell in the moisture

monitor electrolyses the water and measures the amount of water passing through. If the flow-rate is accurately set at 100 cc/min, it shows the reading in "parts per million" by volume. Thus PPM was measured in terms of volume fraction of water in nitrogen at room temperature. Since the nitrogen itself was not moisture-free, a background reading was taken to measure moisture content of the sweep gas so that moisture values could be corrected appropriately.

The temperature of the oven was increased by 10°C for every fresh reading. However, it took a long time to reach a steady-state on the part of the cell - about 8 hours. The steady-state reading of the moisture monitor painter was determined by means of a Sargent Recorder pen which moved both with respect to the pointer and time, as such. A bubble flow-meter measured the exact flow-rate of the purgin nitrogen gas.

(d) Further Refinements

It was obvious from the calculated P vs 1/T semi-log plots that the relation, though expected to follow a typical Arrhenius plot, did not do so. We hence tried to determine the background moisture content as a function of room temperature. When the cylinder was directly connected to the moisture-monitor, it showed the moisture content of the flowing nitrogen gas. At various room temperatures (the laboratory is exposed to fluctuations in temperature) we found a linear relation

between background and ambient temperatures.

The next set of readings were taken with a temperature-dependent background. This temperature is not to be confused with the oven temperature which ranged from 30°C to 90°C, while the ambient ranged from 20°C to 30°C, depending on the weather conditions. This technique produced an exact linear Arrhenius-type plot over the temperature range used. (see Fig. 5).

Solubility: There was not much change in weight (about 1%) when samples of different graft percentages were weighed before and after immersing in tap water at a given temperature for 45 days. The weighing was done every 15 days.

3. Experimental Results

(a) Permeability

(i) Instrumental and Annealing Effects

Styrene contents of the graft films, poly(ethylene-g-styrene), ranged from approximately 1 to 14.7 %, with irradiation times ranging from 1 to 5 hours. We could not work beyond the 5 hour limit due to leakage of air into the system.

In figure 2 irradiation time is plotted versus percentage grafting. Although some individual points are widely scattered (for unknown reasons), the percentage grafting tends to vary directly with the irradiation time and hence linear, as expected. Although annealing of the films before measurement is a preferred procedure, initially, a few films were run without annealing, for the sake of practice.

For a control experiment, we tested the permeability of a 4 mil film of 2" exposure diameter for its permeability constant at various temperatures ranging from 25°C to 80°C. As described before, the moisture monitor recorded the moisture content of the purging nitrogen gas and the rate at which it was purging.

When log permeability was plotted against the reciprocal of absolute temperature (°K), the permeability curve for a plain, unirradiated, ungrafted polyethylene film showed a transition region at 54°C, the 54°C point being the region where the slope of the straight line graph changed abruptly (see figure 3). It was not known immediately if the transition was real or spurious. In some cases, transi-

tions in permeability constants have been related to the glass transition. However, polyethylene does not exhibit a transition in this range of temperature.

Expecting to see a similar curve for a grafted film, we ran a 11.2 % styrene graft film in tap-water, but found no transition. In order to check the validity of the observation, we checked the moisture-content of the nitrogen gas (background) from the cylinder as a function of ambient temperature. As the room-temperature changed very little during this period, we could only get a few close points of PPM (background) as related to the temperature.

Surprisingly, a linear relation between moisture content and temperature of 20°-30°C held, and was used to give a corrected background value (Fig. 4). We thus corrected for non-isothermal laboratory conditions. Application of this correction to a 11.2 % styrene graft film gave a single straight line (Fig. 6). Thus, a transition appears only if we assumed a constant background, and is thus apparently spurious. All further experimental values were corrected for the effect of temperature on background moisture content.

Having corrected for background, we used the same film (which was being slow cooled from a previous high of 80°C) to a room temperature of 25°C, taking a full 24 hours for this in-line annealing. On being re-run, the 11.17% graft gave a remarkably reproducible graph, which only vaguely differed from the previous result.

A new control sample of polyethylene (annealed at 70°C for 24 hours) was run to establish a comparison of the grafts. The curve

for the 11.2 % styrene sample very nearly coincided with the control line, within experimental error, with a slightly higher activation energy (Ep).

In order to further improve the usefulness of the graft copolymers, we tried to alter the crystalline structure of the films by annealing. If the morphology could be altered in a manner that would provide more resistance to permeation, this could considerably reduce the permeability to water.

The subsequent films (including the twice used 11.2 % styrene content film) were annealed in a tap-water bath at 70°C for 24 hours. After 24 hours, they were slowly cooled for about 2-3 hours to about room temperature. The films were dried and immediately used for the experimental runs. A temperature of 70°C is above the glass transition temperature of polyethylene, but below that of polystyrene. Hence, the annealing procedure might be expected to result in an annealing and shrinkage of polyethylene around the polystyrene portions.

(ii) Effects of Grafting on Permeability and Other Properties

Permeability:

As mentioned, the permeability curve of the 11.2 % styrene film was only slightly lower than that of the control curve. The following table indicates the computed values for all specimens.

Table 1.

Percentage grafting	Code Name	Ep, Kcal/mole	Remarks
0	1B	16.8	Control
11.2	2A	15.8	Unannealed
11.2	2B	15.8	Annealed
11.7	3A	16.0	"
14.7	4A	14.1	"
8.6	3A	16.3	"
7.2	6A	13.9	"

Solubility:

An attempt was made to run solubility tests for a few films by immersing the films in water-baths at various temperatures for about 2 months.

Films of various graft compositions and of about 1 square inch in area were weighed and immersed in different water-baths at various steady-temperatures. The temperatures were at 25°C, 50°C, 68°C and 100°C. Wherever necessary, a condenser was attached to condense back the escaping vapors. However, since many of the films were light, they tended to float rather than be submerged and presented only one side to the water surface. Films were weighed every 15 days, but showed no appreciable gain. In some cases, there was a loss of weight, indicating an extraction process. Hence, some films were left for a short time as 23 days whilst some at a lower temperature were left for as long as 60 days. Clearly, consistent relationships

were not observed, perhaps due to differences in morphology. The graphs are shown in Figure 13.

Density Measurements:

The densities of the films (gm/cm^3) when plotted against the percentage grafting, showed a maximum. The density of the control showed 0.9745 gm/cm^3, a comparatively higher value for polyethylene. An ungrafted, but irradiated, film of polyethylene (irradiated 6 hours) showed a density of 0.9690 gm/cm^3. The highest density value recorded was that for a 6.25% film - 1.175 $gm./cm^3$. Figure 12 is self-explanatory.

Morphology:

Transverse sections of a control film and a 14% film were microtomed to a thickness of 25 microns and studied under a polarizing microscope. Not much difference was noted with respect to the control and the styrene grafted film.

4. Discussion

There are two major questions to be discussed:

(1) Why does the density of the graft polymers go through a maximum as the percentage of styrene grafted increases?

(2) Why doesn't grafting of styrene decrease the permeability of polyethylene to liquid water?

(a) Effect of degree of grafting on Permeability

Ballantine et al (2) have considered the method of pre-irradiation in vacuo as the preferred method for the synthesis of the most homogenous graft co-polymers of polyethylene and styrene. They also comment that the trapped free radicals are trapped in the crystalline regions rather than in the amorphous regions where they could be mobile enough to recombine. It is generally considered by them that irradiation beyond a minimum value decreases crystallinity.

Fels and Huang (5) say that the grafting of styrene to polyethylene produces a greater impediment to permeation of gases than the crystalline regions in polyethylene. Even though some disruptions of the crystallite regions may occur due to grafting, the reduction in permeability due to grafting appears to predominate so that grafting results in an overall reduction in P.

Huang and Jarvis (9) suggest that in the separation of water from organic liquids using polymer membranes, water acts as a plasticizing agent. Thus water swells the polymer, loosens it, and allows polymer segments to move freely about the backbone. Water also

forms "clusters" in which case resistance to transmission is built up. They feel that only the amorphous regions take part in the transport processes.

Myers and Stannett (7) report that a minimum exists for P with respect to gases when styrene is grafted to polyethylene in various percentages. After a certain percentage P starts increasing. At low percentages of styrene, a dense interpenetrating system of polyethylene and polystyrene is formed, so that a tight "fortress" is developed. Later, as the styrene percentage increases, the polystyrene segments formed in the amorphous regions can disrupt the crystalline regions.

The minimum P noted by Huang et al (8) was for grafts having between 20 and 30% styrene. Huang and Kanitz speculate that structural changes which strongly affect P could be arising out of a filling up of the free volume and a subsequent decrease in segmental mobility, at least initially. Later, at higher percentages of styrene, the increase in P is probably caused by changes in the amorphous/crystalline ratios. At 20-30% grafting, the grafted polystyrene chains penetrate and disrupt some of the crystalline regions of the polyethylene and open up new regions which are available for permeation. Thus, permeability increases at high degrees of grafting.

Fujita (3) feels that perhaps the free volume theory fails for water molecules as penetrants as he cites examples of polyvinyl acetate-water and PMMA-water. Diffusion of small molecules such as

water require for their jumping only a very local co-operation of the solid-like vibrations of 2 or 3 monomers and, therefore, their rate of diffusion would not depend on physical factors through the average free volume theory of the system. It would simply increase with temperature as a result of enhanced thermal vibrations of individual monomers and the penetrant molecules.

(b) Possible Explanations

It is quite possible that what we had been attempting could hold good only for gases and larger-diameter liquids. Perhaps the water molecule, being very small, can penetrate relatively easily regardless of filling up the free volume. This explanation would be consistent with the suggestions of Fujita (3).

A second reason for the behavior observed could be based on observations by Michaels and Bixler (15), who say that annealing a film in a particular liquid will make that liquid a highly-preferred penetrant molecule. Perhaps this is what happened with our films when we annealed them in tap-water for 24 hours at 70°C.

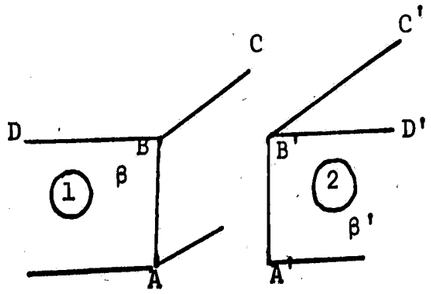
A third factor to consider is the process by which we grafted our films in contrast to the ways other workers prepared their films. Ballantine et al (2) say that pre-irradiation in vacuo, followed by the actual grafting mechanism could lead to the most homogeneous type of grafts of the said films. Other workers studying the permeability of grafted films, have followed the simultaneous irradiation-cum-grafting procedure. Such films are slightly less homogeneous, and their permeability coefficients have minima around the 20-30% styrene graft region. For more homogeneously grafted

films, the minima could well exist in a region of styrene concentration very much below the 20-30% level.

Thus in effect, following the Ballantine technique, we have probably prepared more homogeneous films than other workers. It is possible then that the grafted polystyrene is already outgrowing the free-volume space and protruding into the crystalline regions at styrene concentrations well below the 20-30% range.

Still another possibility is that the films are not homogenous, in spite of use of the Ballantine technique-thus exhibiting no reduction in P, at all. If the density graph is studied, Fig. 12, it is possible to speculate on the morphology of these films as follows:

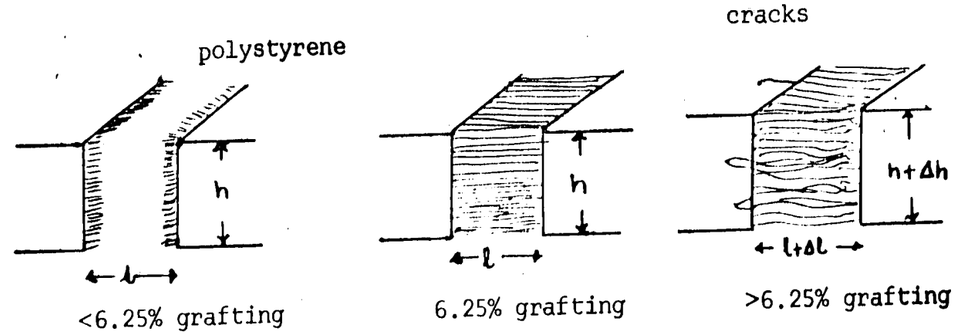
Imagine that free-radicals form on the interface of the crystalline-amorphous region and suppose they survive and easily attach themselves to styrene molecules because of lower mobility of the former in the crystalline regions. We are supposing that free-radicals have more mobility in the amorphous region so that they can preferentially combine with each other rather than with styrene. If polystyrene could grow in random directions, could the following hold true?



1, 2 are crystalline blocks. Region between 1,2 is amorphous.

Plane ABD (plane β is the film-side that faces us. So is plane β' facing us. Between planes α and α' (not shown in figure), lies the amorphous region. Let us call it a 3-dimensional space "S". Polystyrene chains could grow in this region, and possibly we can explain our density phenomenon through this growth.

With reference to the density curve (fig. 12) it is possible to explain the phenomenon as follows. At less than 6.25% of the styrene grafting, the polystyrene chains grow in random directions and try to fill the amorphous regions with grafted polystyrene. As in the figures below, the process is like a liquid filling up a vessel and then setting to a solid



<6.25% grafting 6.25% grafting >6.25% grafting

At 6.25% grafting, a number of free radicals exist, which is larger than for the less-grafted films. Thus, more chains can grow and they completely fill the amorphous region, i.e., the free volume Neglecting any disruption of the crystallites up to the grafting level of 6.25%, and also neglecting surface and outward growth, we can say a maximum filling up of the free volume has occurred.

After this maximum has occurred, if further styrene is to be grafted (for a still larger number of free-radicals generated by larger exposure in the gamma-cell), the growing polystyrene chains and freshly beginning chains exert an influence on the crystalline walls. A wedge shaped entrance starts forming, widening to equal width throughout as grafting is completed. Thus, we have a volume space greater than the actual volume S. Cracks could also develop on the crystalline walls. It is quite possible that a hole now exists, which could not have existed at an optimum 6.25% (ideal optimum). This decreases density and increases permeation of liquids.

In fact, we have an increased permeation than for the control, suggesting that a bigger hole now exists than for plain polyethylene.

It is apparent that the above proposed model might not exist in our samples-in the sense that disruptions could have started at a much early stage. Also, the pores could have widened much earlier. The permeabilities of grafted polyethylene films is more than or equal to that of the controls, if not less. Nevertheless, a practical investigation for the feasibility of a near-ideal model is desired. A thorough knowledge of the morphology during polystyrene build-up could help us in synthesizing a more suitable barrier film for the protection of concrete in the desalination process.

5. Acknowledgements

The following have greatly assisted in the materialization of this report:

Dr. J. A. Manson	Professor in Charge Director of Polymer Laboratory Lehigh University Materials Research Center
Dr. M. F. Abd-El-Bary	Research Associate

Mention should be made of Dr. R. W. Coughlin of the Department of Chemical Engineering for kindly permitting the use of the gamma-cell.

Thanks are due to the MRC secretaries, Mrs. Benzak and Mrs. Maioriello for assisting in the preparation of the final transcript.

The project was funded by the Office of Saline Water, Grant No. 14-01-0001-1714, and the support is gratefully acknowledged.

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4. A. J. Connolly, J. Materials, 5:339 (June 70).

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14. P. J. F. Kanitz, R. Y. M. Huang, J. Appl. Poly. Sc., 14, 67 (1971).

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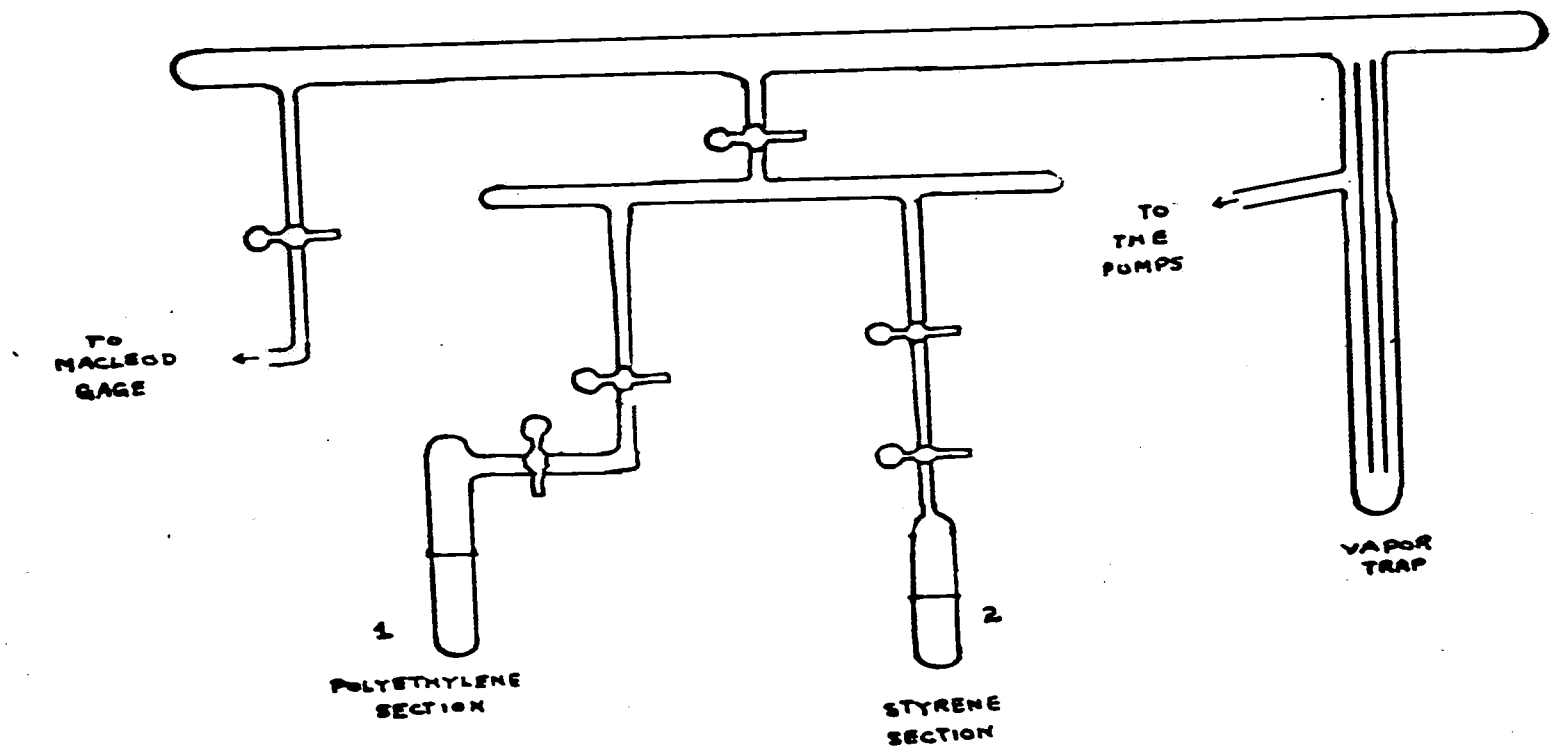
Fig. 1. The vacuum system in which deaeration and post-irradiation styrene contact with polyethylene took place.



THE VACUUM SYSTEM

FIG. 1

Fig. 2. Plot of irradiation time in the Gamma Cell 220 and the corresponding styrene grafting that resulted.

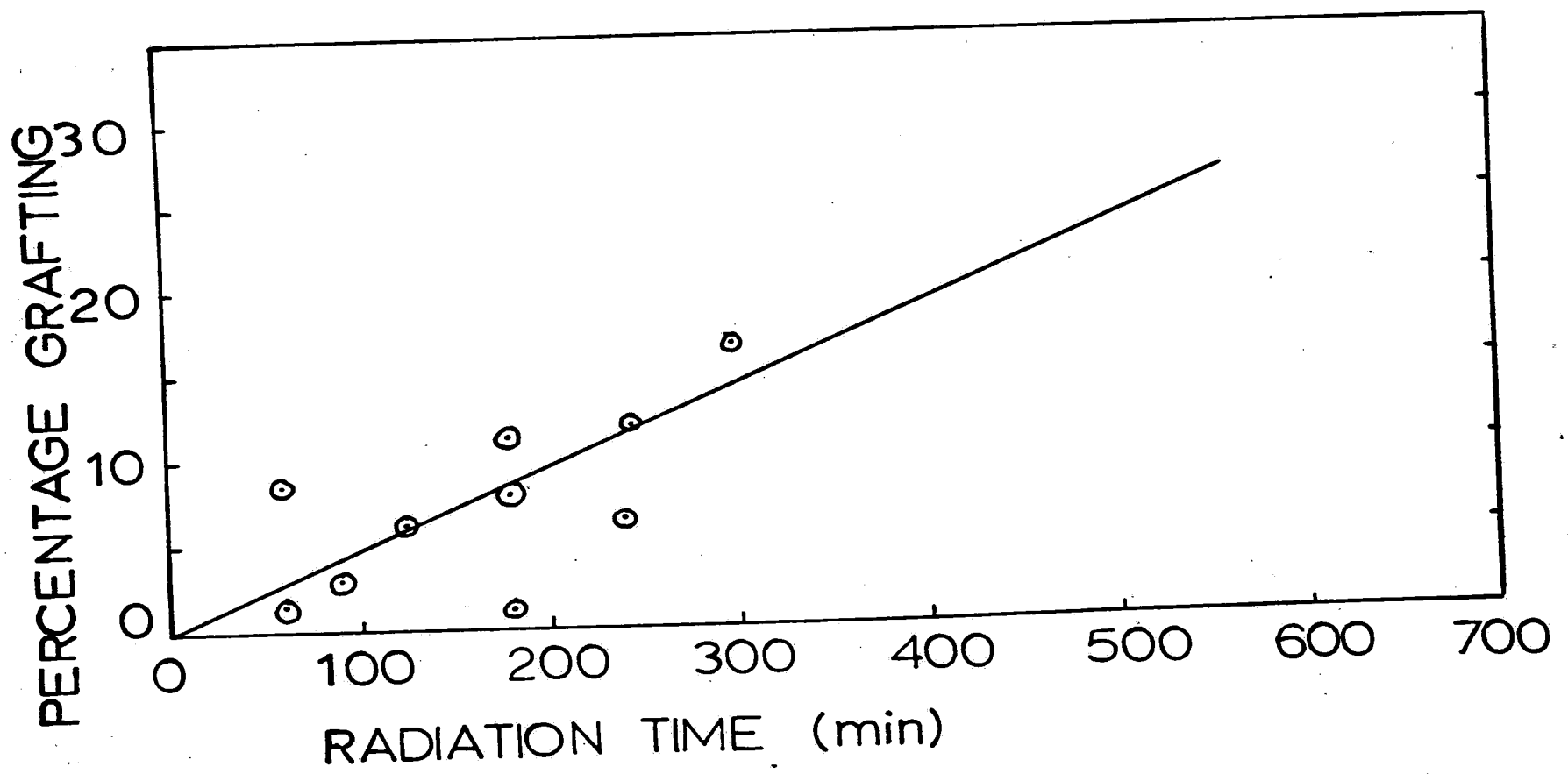

PERCENTAGE GRAFTING
30
20
10
0
0
100
200
300
400
500
600
700
RADIATION TIME (min)

FIG. 2

Fig. 3. Permeability of control and 11.2% styrene grafted polyethylene plotted against reciprocal absolute temperature. For the control, background deducted was not a function of ambient temperature.

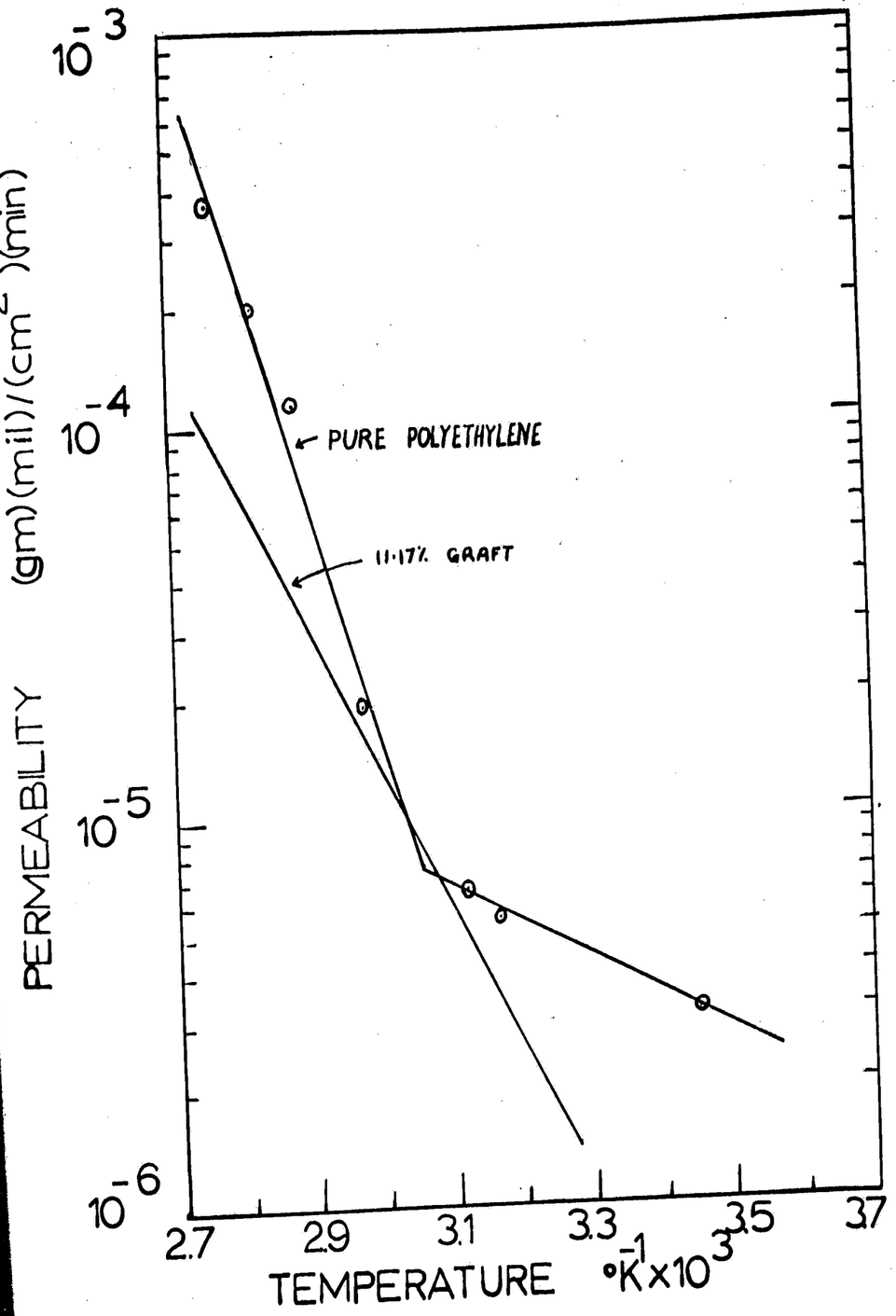

PERMEABILITY (gm)(mil)/(cm^2)(min)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
PURE POLYETHYLENE
11.17% GRAFT
2.7
2.9
3.1
3.3
3.5
3.7
TEMPERATURE °K^{-1} x 10^3

Fig. 4. Background (PPM) plotted against ambient temperature (^{o}C).

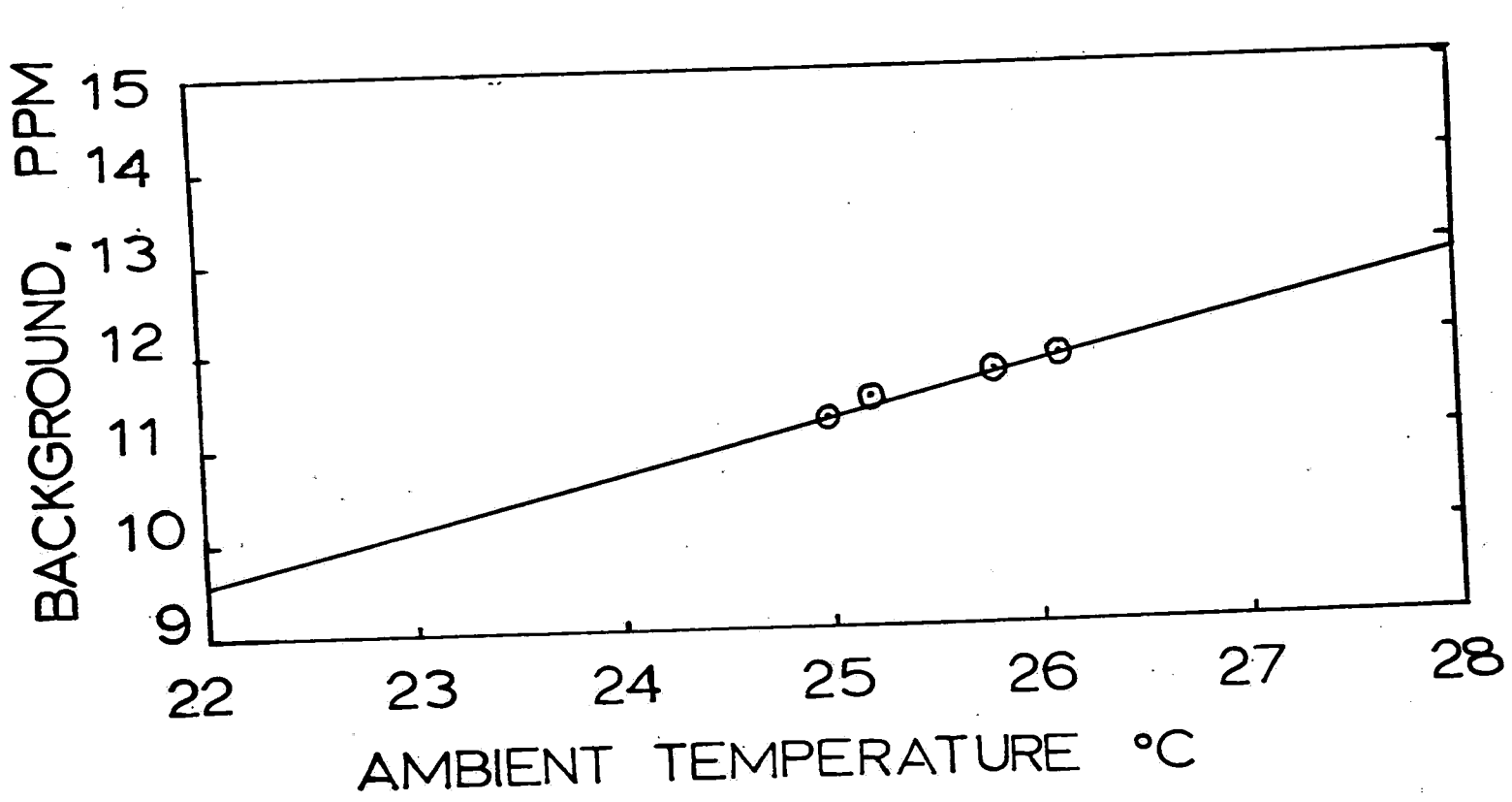

BACKGROUND, PPM
15
14
13
12
11
10
9
22
23
24
25
26
27
28
AMBIENT TEMPERATURE °C

Fig. 5. Control annealed. Permeability of control.

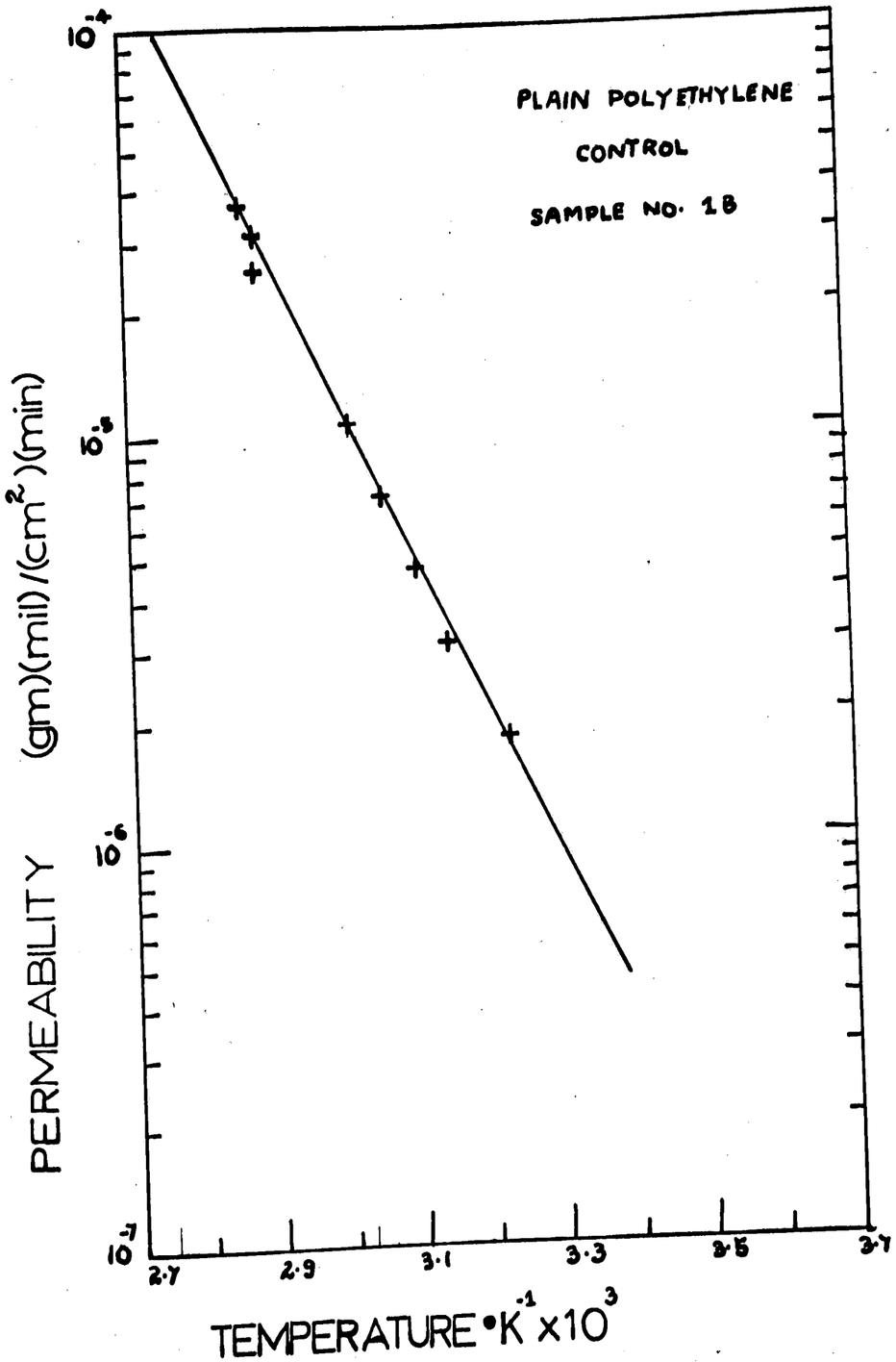

PLAIN POLYETHYLENE
CONTROL
SAMPLE NO. 18
PERMEABILITY
(gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ x10³

Fig. 6. Permeability of an 11.2% styrene graft, annealed.

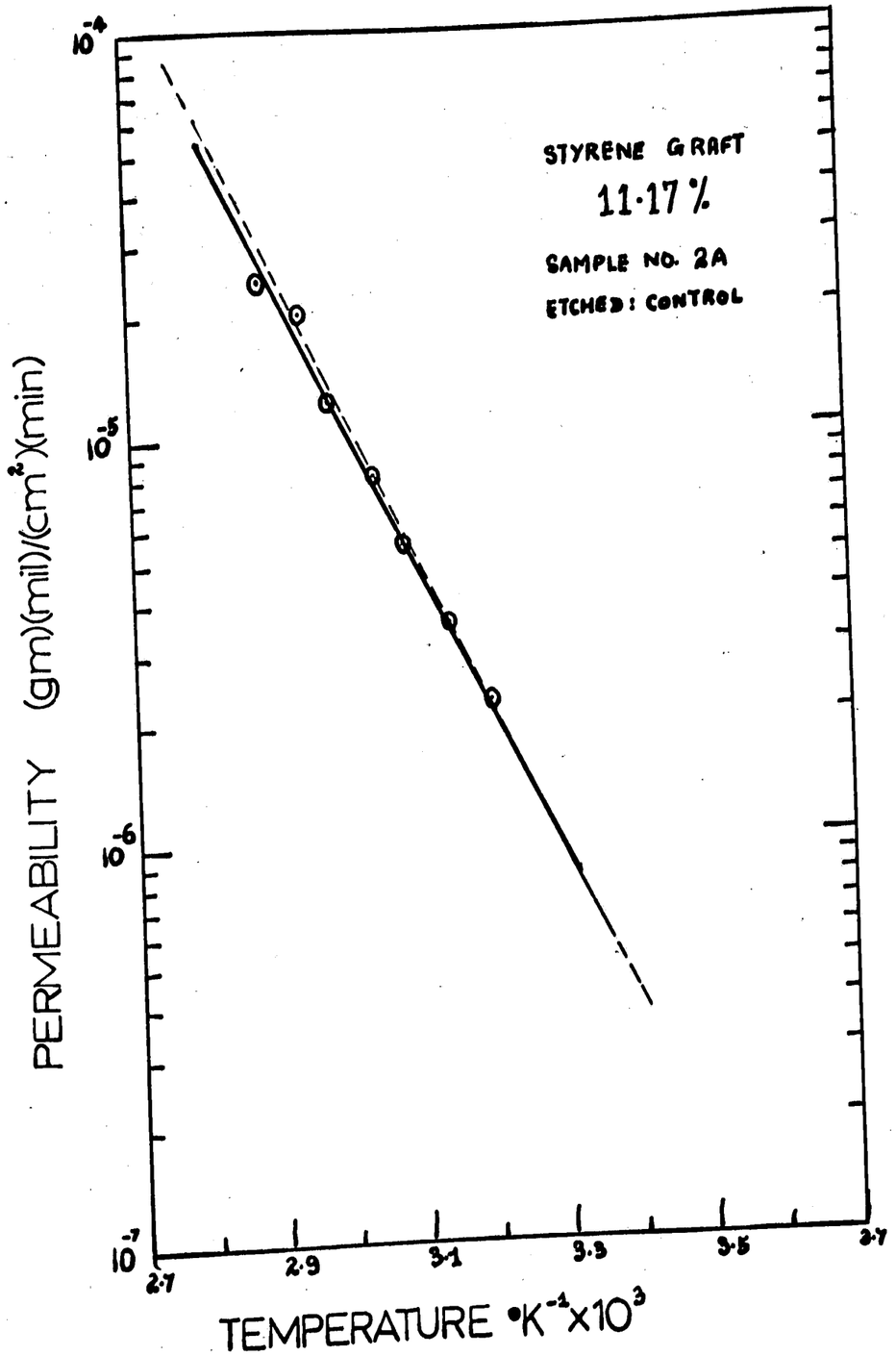

STYRENE GRAFT
11·17 %
SAMPLE NO. 2A
ETCHED: CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ X 10³

Fig. 7. Permeability of an 11.7% styrene graft.

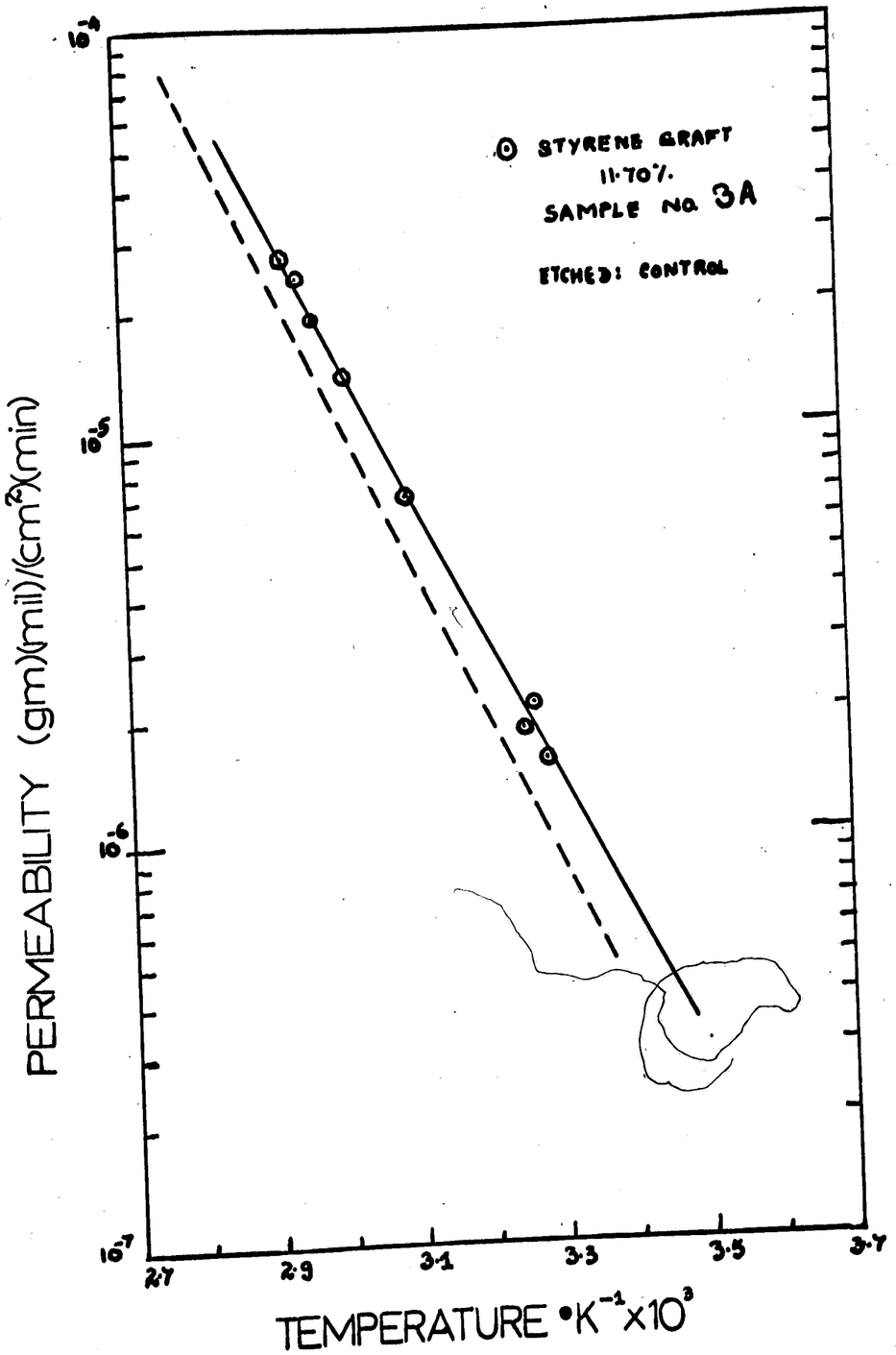

⊙ STYRENE GRAFT
11·70%.
SAMPLE NO. 3A
ETCHED: CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹×10³

Fig. 8. Permeability of a 14.7% styrene graft.

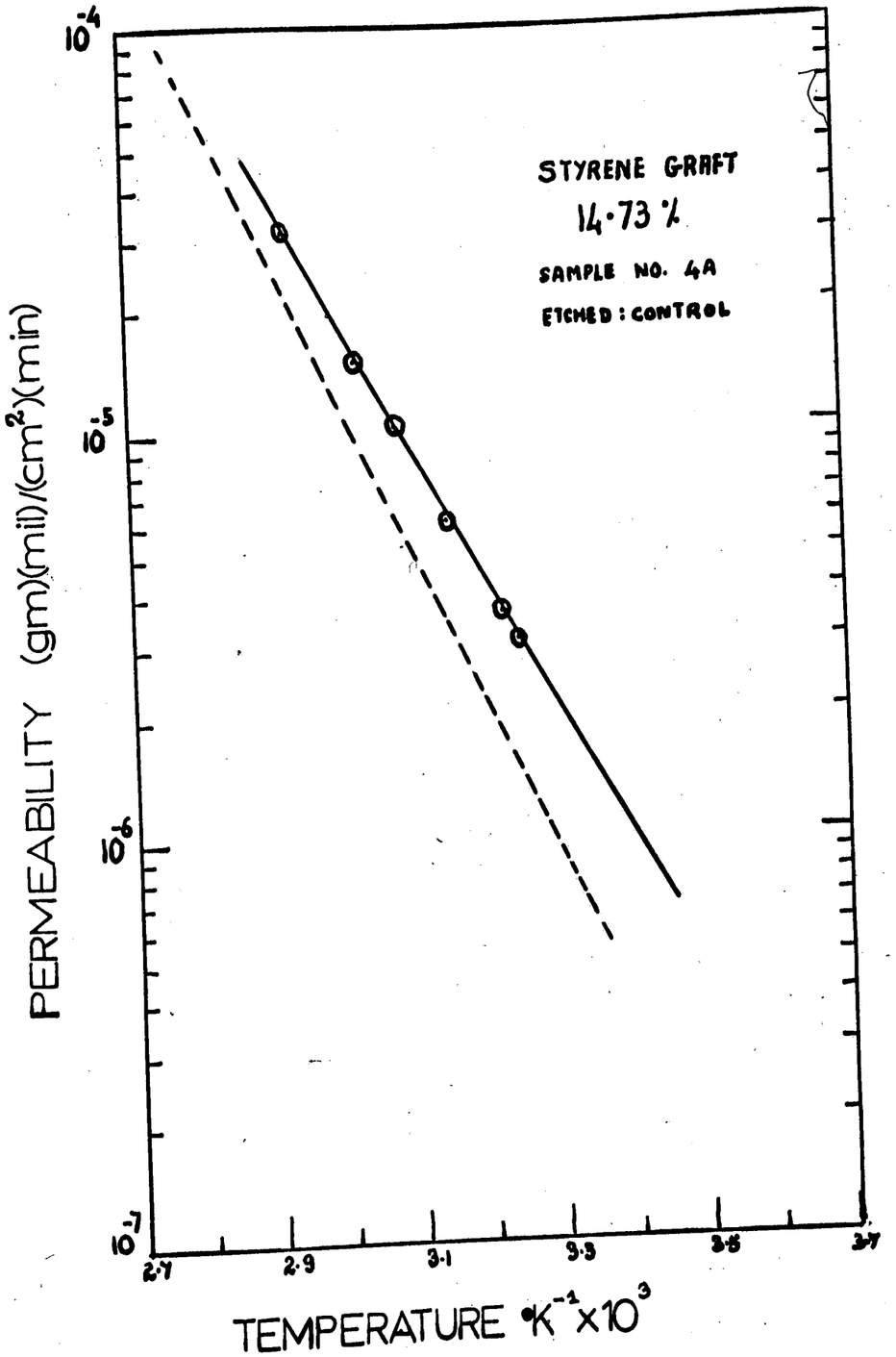

STYRENE GRAFT
14·73 %
SAMPLE NO. 4A
ETCHED : CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ X10³

Fig. 9. Permeability of a 11.2% styrene graft. Sample 2B is the same as 2A, but annealed in line due to constant use.

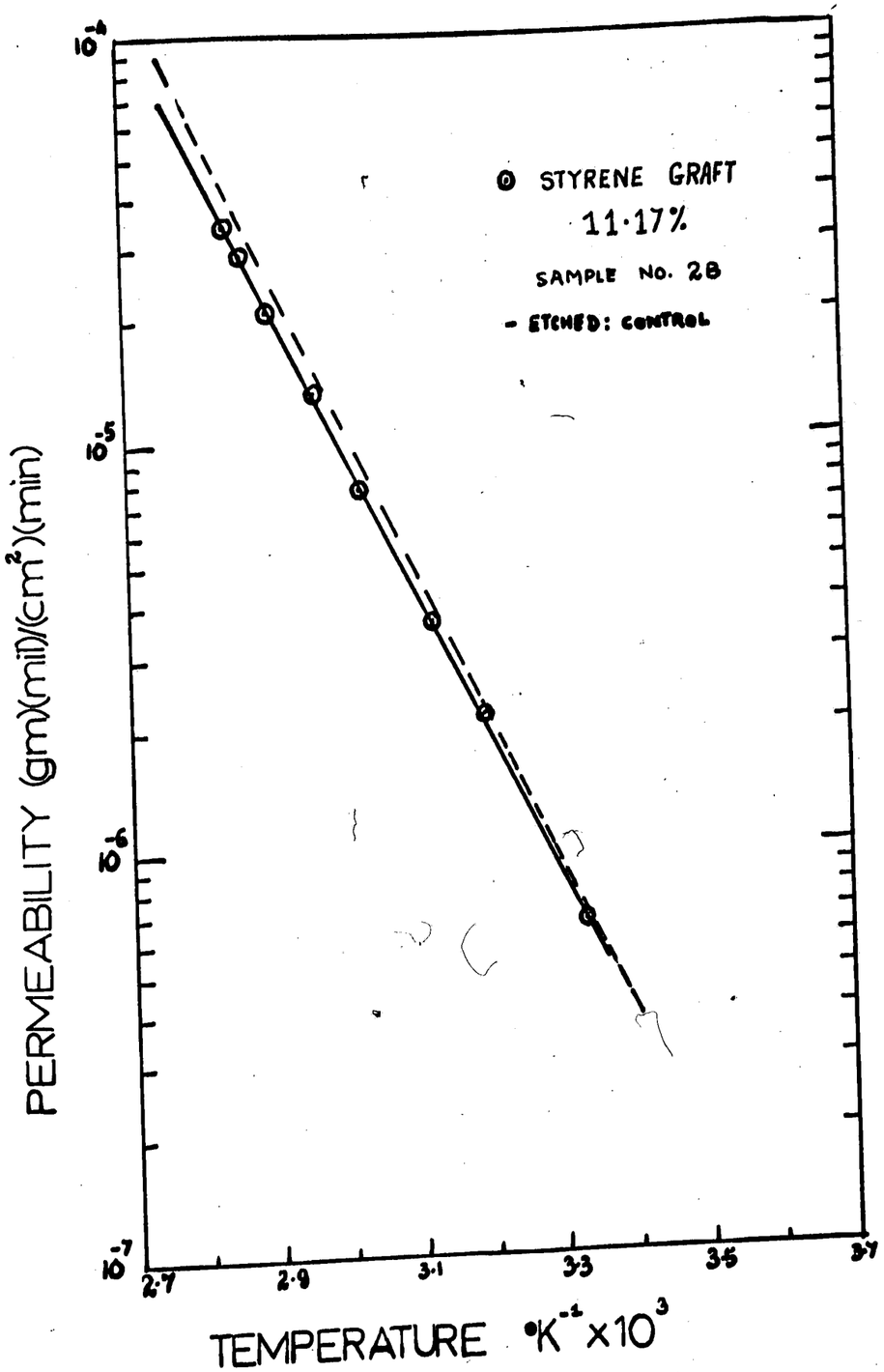

STYRENE GRAFT
11·17%
SAMPLE NO. 28
- ETCHED: CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ x 10³

Fig. 10. Permeability of a 8.6% styrene graft.

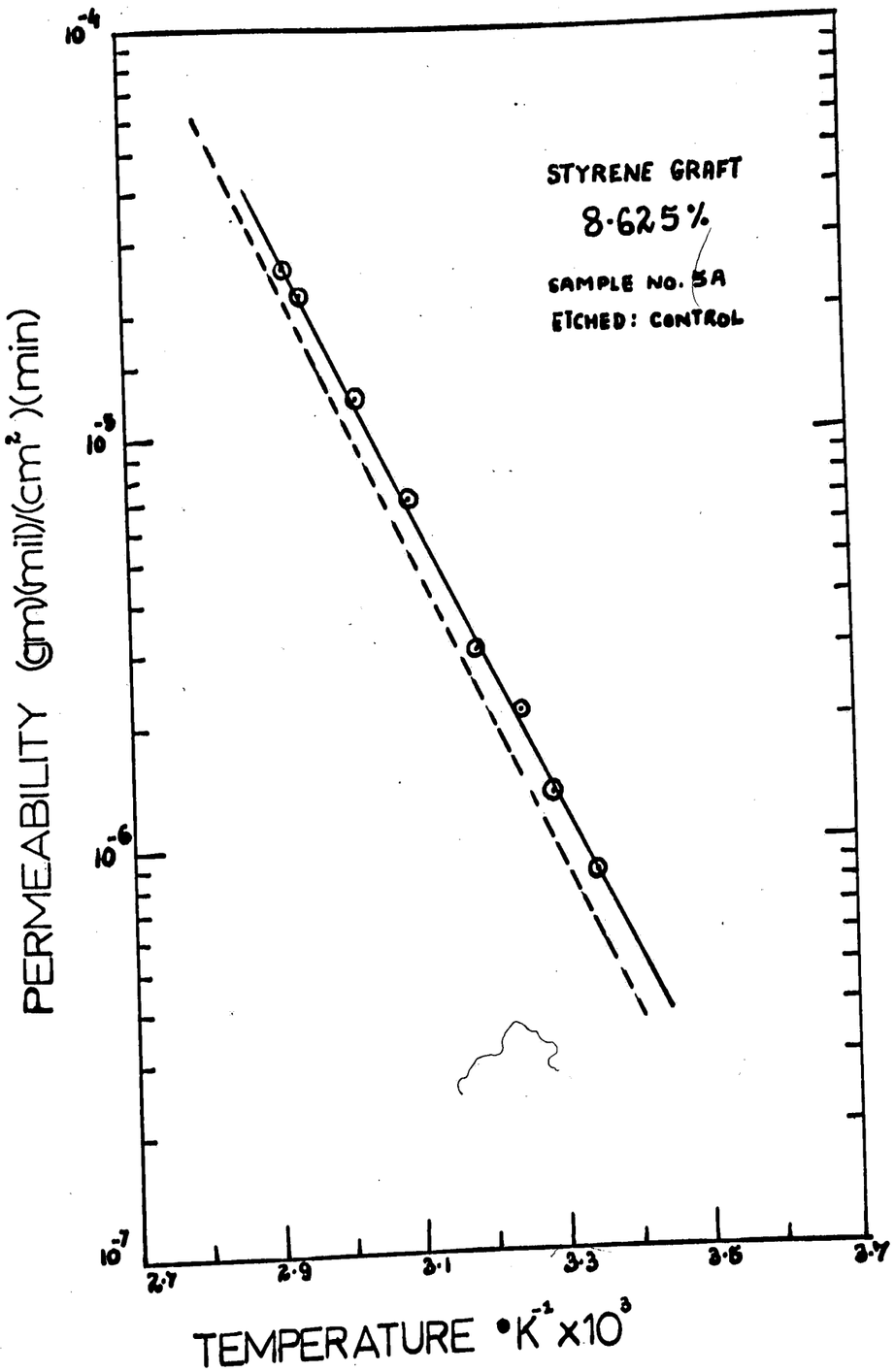

STYRENE GRAFT
8·625%
SAMPLE NO. 5A
ETCHED: CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ x10³

Fig. 11. Permeability of a 7.2 % styrene graft.

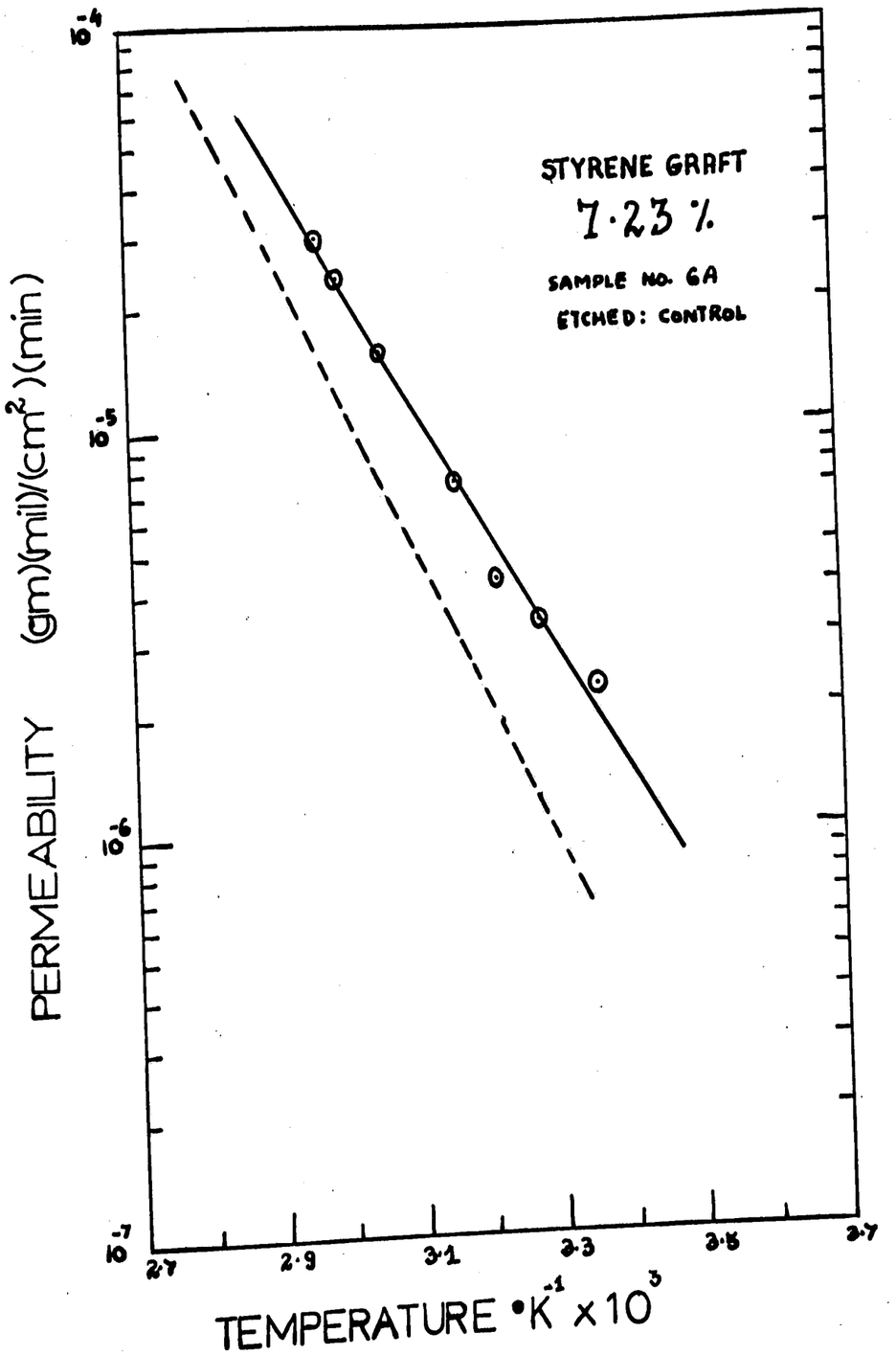

STYRENE GRAFT
7·23 %
SAMPLE NO. 6A
ETCHED: CONTROL
PERMEABILITY (gm)(mil)/(cm²)(min)
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
2·7
2·9
3·1
3·3
3·5
3·7
TEMPERATURE °K⁻¹ x 10³

Fig. 12. Density of polyethylene-styrene graft polymer as a function of styrene graft percentage.

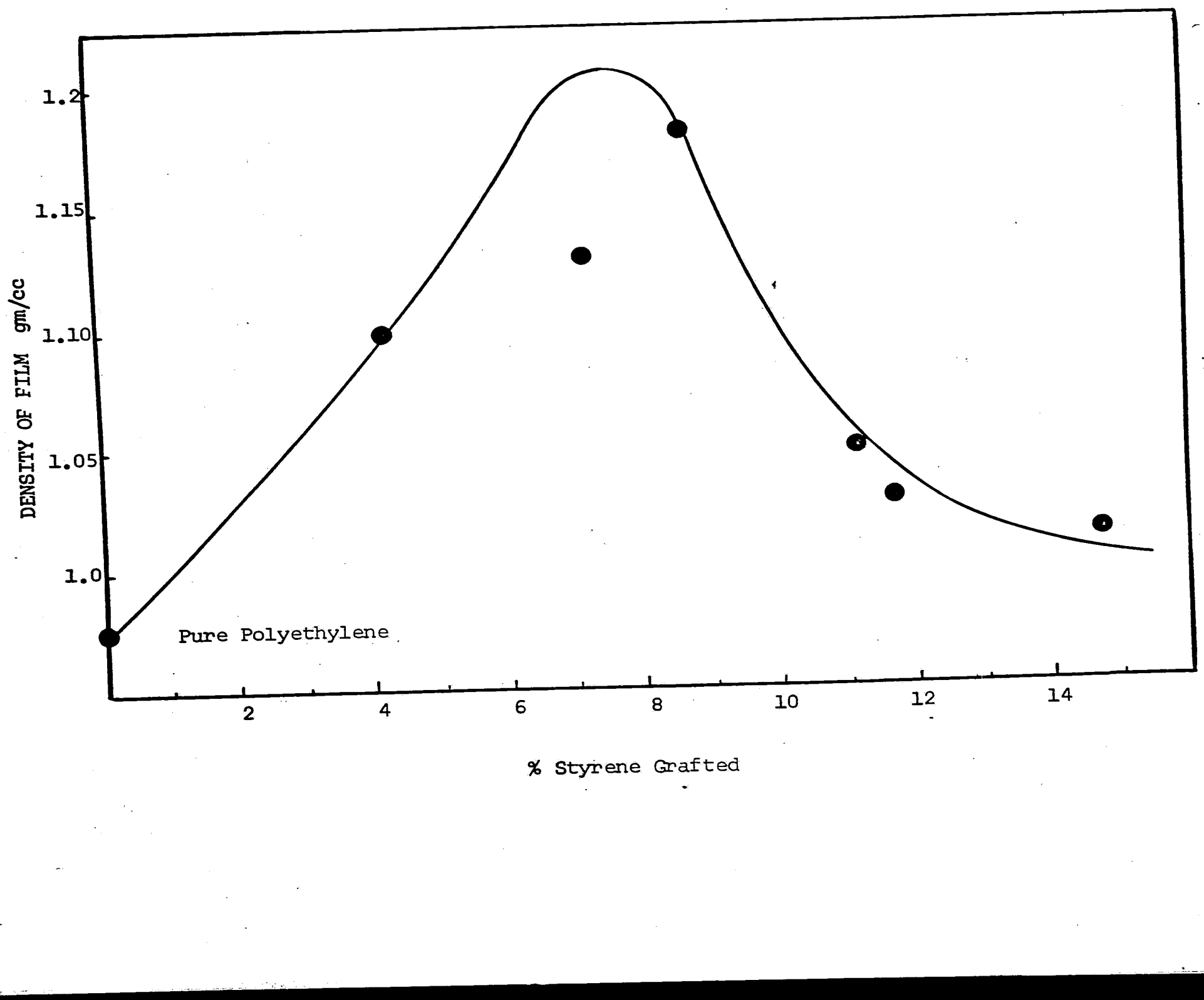

1.2
1.15
1.10
1.05
1.0
DENSITY OF FILM gm/cc
Pure Polyethylene
2
4
6
8
10
12
14
% Styrene Grafted

Fig. 13. Solubility (gm/100 gm) of grafted polymers against temperature (^{o}C). Solubility tests carried out for a maximum of two months.

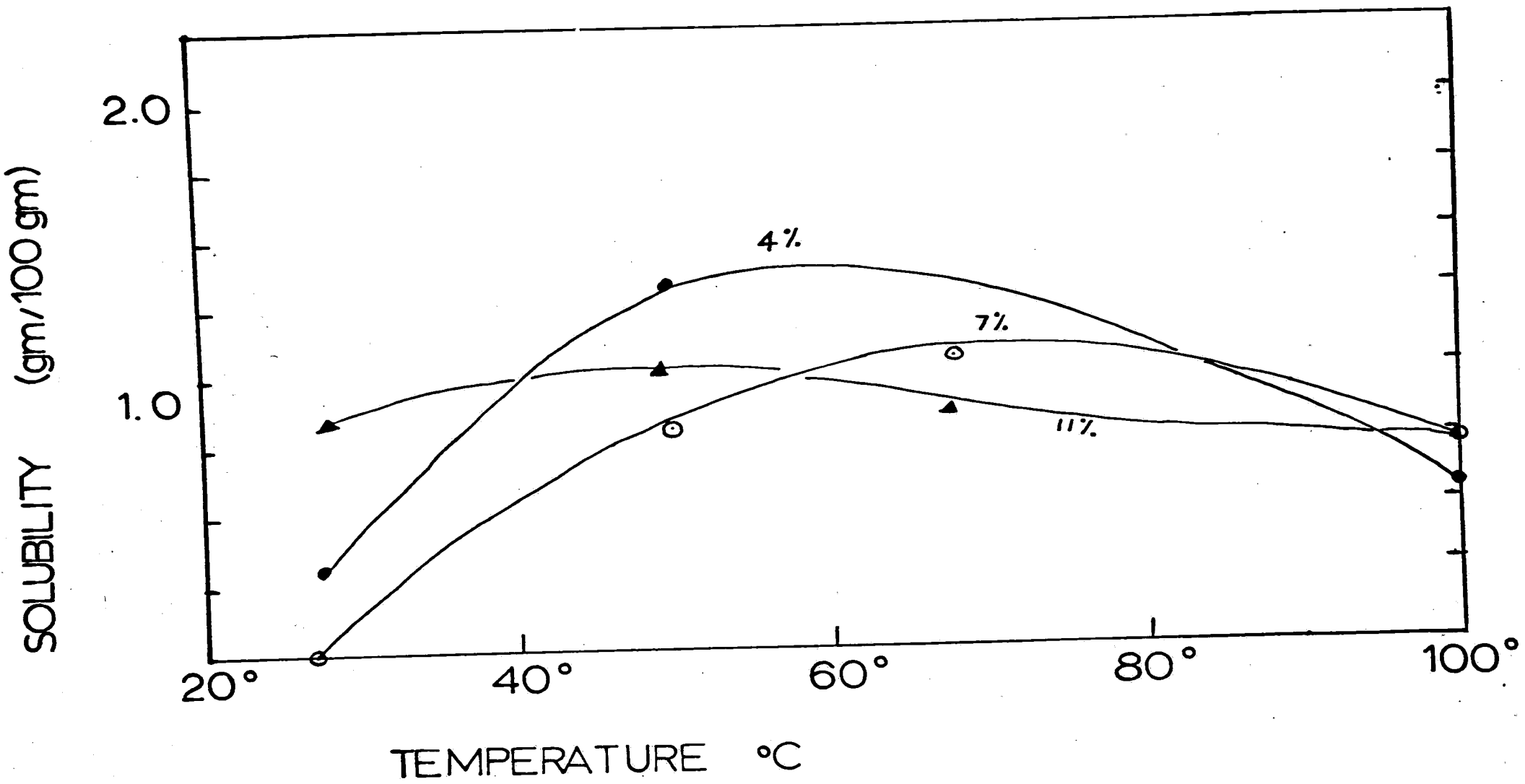

SOLUBILITY (gm/100 gm)
2.0
1.0
4%
7%
11%
20°
40°
60°
80°
100°
TEMPERATURE °C

TABLE 1.

Kinetic Parameters for Permeation for Polyethylene-Styrene Grafts.

$$P = P_o e^{-E_P/RT}$$

$$\log P = \log P_o - \frac{E_P}{RT} \log e$$

$$\log P = \log P_o - \frac{E_P}{R} \times \log e \ \frac{1}{T}$$

Sample No.	Graft Percentage	E_P, $\frac{kcal}{mole}$	Equation of line = $A - \frac{B}{T}$
1A	0	16.8	$6.11 - (3682.8)\frac{1}{T}$
6A	7.2	13.9	$4.50 - (3043.2)\frac{1}{T}$
5A	8.6	16.3	$5.87 - (3569.1)\frac{1}{T}$
2A	11.2	15.8	$5.41 - (3457.5)\frac{1}{T}$
2B	11.2	15.8	$5.42 - (3473.4)\frac{1}{T}$
3A	11.7	16.1	$5.75 - (3515.1)\frac{1}{T}$
4A	14.7	14.1	$4.52 - (3085.1)\frac{1}{T}$